



Comparison of precious metal oxide/titanium monolith catalysts in wet oxidation of wastewaters

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ABSTRACT

CWO (catalytic wet oxidation) of a process wastewater and phenolate solution was carried out at 230 °C, 200 °C and total pressure of 50 bar, with oxygen, in a stainless steel autoclave. Monolith Ti mesh supported precious metal oxide catalysts were characterized with XPS, ICP-MS, SEM and their activity compared in oxidation of model and real wastewaters.

The Ru/Ir oxide coated Ti monolith catalysts showed remarkable catalytic activity in wet oxidation both in the overall oxidation expressed by COD (chemical oxygen demand) decrease and in the carbon mineralization expressed by TOC (total organic carbon) decrease. This was valid for the real pharmaceutical wastewater as well as for a phenolate solution too. Meshes containing Ru, Pd and Ir oxide alone were less active than Ru/Ir together on Ti. This observation is in accordance with the electrochemical properties of the same mesh used in hypochlorite production.

The commercial mesh was most stable under the conditions of wet oxidation, however the loss of its precious metal content was observed during longer usage. The Ru/Ir monolith catalysts prepared in our laboratories had similar initial activity but they were less stable, the leaching and/or abrasion of the surface precious metal oxide layer was faster, independently of that their had fragmented or continuous structure, resulting from the preparation methods.

The loss of activity during longer usage can be the result of deposition of iron and silicon oxides too, as showed by SEM (scanning electron microscopy) analysis.

An important feature of the good catalytic activity of the Ru/Ir oxide coated Ti mesh can be the uniform distribution of the two oxides showed by LA-ICPMS (laser ablation-inductive coupled plasma mass spectrometry). According to XPS (X-ray photoelectron spectroscopy) results, the upper surface layer of the catalysts is covered by a mixture of Ru–Ir–Ti oxide of approximately 0.1:0.02:1 atomic ratio for commercial catalyst, and an 0.5:0.7:1.0 atomic ratio for catalysts prepared in our laboratories. We suppose that such mixture of oxides with uniform distribution are the carrier of the good catalytic activity.

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1. Introduction

Wet (air) oxidation (WAO) is a well-known process for the treatment of industrial process wastewaters and mother liquors, by which the pollutants are converted into easily biodegradable substances or completely mineralized. The catalytic version of WO, CWO permits to lower the temperature and pressure of the reaction.

Catalytic wet (air) oxidation has been applied to many different model effluents and some complex industrial wastes [1–6]. Three rather detailed reviews described wet oxidation and catalytic wet oxidation [7–9] of wastewaters, including that of some industrial process wastewaters.

Soluble transition metal salts (such as copper and iron salts) have been found to give significant enhancement to the reaction rate, but a post-treatment is still needed to separate and recycle them.

Heterogeneous catalysts have the advantage of easy separation. Mixtures of metal oxides of Cu, Zn, Co, Mn, and Bi are reported to exhibit good activity, but catalyst leaching was detected [1,2]. On the other hand, heterogeneous catalysts based on precious metals deposited on stable supports are less sensitive to leaching [3,4]. Pt

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and Ru on ceria and zirconia–ceria supports [5,6] were tested in oxidation of acetic acid. Activity of Ru oxide on different oxide supports in acetic acid oxidation was recently reported. The catalyst supported on mixed Zr, Ce oxide proved to be most active [7]. During CWAO of formic acid, acetic acid and phenol, which was carried out in a trickle bed reactor over various Ru/TiO₂ catalysts, complete oxidation of formic acid was obtained and no catalyst deactivation was observed. As a result, Ru/TiO₂ catalysts were proved to be active for total conversion of phenol. On the other hand a lower conversion of acetic acid was detected, due to oxidation of metallic Ru to RuO₂. This observations and the stability of Ru–Ir oxide coated Ti mesh in strongly oxidative environment initiated our work with the precious metal oxides coated Ti meshes.

Highly concentrated process waste waters (PWW's), mother liquors of chemical, pharmaceutical production often cannot be treated directly or even in diluted form with biological treatments, because they might be toxic and/or non-biodegradable, so there is a significant need for wet oxidation. Catalytic W(A)O has been applied more frequently to different model effluents than to real and complex industrial wastes [8–10,3,4].

Similarly few data are available about the activity and stability of catalysts used in WO of real industrial process wastewaters [11,7–9,12]. Without such knowledge their use in large scale operation is, however difficult. Powder form precious metal oxide on titania catalysts and a commercial monolith Ti supported Ru/Ir oxide catalyst were tested in our laboratory [13,14], aimed primarily at revealing of the oxidation properties of the real process wastewaters. In the present paper the results of characterization and activity comparison of different precious metal oxides coated Ti mesh monolith catalysts are presented. The precious metal composition and the method of preparation were varied, the catalysts were tested in the oxidation of a real and a model wastewater, the latter one containing phenol.

2. Experimental

2.1. Catalyst preparation

The commercial mesh catalyst (Ru–Ir oxide coating, from Magneto Bv, The Netherlands) was used as received, its size was 500 mm × 100 mm, mass 73 g (No 1, 1(2), fresh, two samples from different parts of the mesh; No 1(3), used). The two other catalyst types (4–9) were prepared in our laboratory from a Ti mesh delivered by Baoji Titanium Industry Company, Shaanxi, China, also 500 mm × 100 mm, its mass was 170 g. The specific mass difference was originated from the different thickness and gap-metal ratio of the two meshes. The surface ratio of them was calculated supposing square cross section of their elements, the ratio was Baoji/Magneto ~1.5

The first step of the preparation methods was (A) chemical purification or (B) mechanical purification. Preparation (A, samples 4–7): the first step was a degreasing with acetone solvent and water washing. This was followed by etching with a mixture of strong acid (HCl) and H₂O₂. Finally the oxide coating was developed by wetting the pretreated mesh with 1% isopropanolic solution of the precious metal salt (that of Pd, Ru and/or Ir), followed by drying and calcination at the first layer at 600 °C (in order to ensure the intensive interaction between titania layer and precious metal oxides) at the second and third at 450 °C. The mechanical purification (B, samples 8 and 9) was sand-blasting, which was followed by wetting the pure mesh with 1% aqueous solution of Ru and/or Ir chloride (Ta), drying and calcining in air at 450 °C, repeating the above described procedure for 5 times. As the comparison of activity of supported precious metal oxides was aimed, no reduction of the catalysts occurred.

2.2. Catalyst characterization

The amount Ru, Ir (Ta) and Pd content is one of the most important parameter of the monolith catalysts. For the determination of the precious metal content several options were considered, finally after having excluded the analytical methods which were associated with the dissolution of catalyst samples, the prompt gamma activation analysis (PGAA) was chosen. This method analyses the sample as received, and the measuring device is available in our institution attached to the research nuclear reactor. Another argument favoring this technique was that besides the metals it showed the carbon content (if any) of the catalysts also. The error of C content measurement is rather high, as the sensibility of PGAA for carbon is low. Another uncertainty is originated from the mode of measurement, the pieces of meshes had to be placed into a PTFE (polytetrafluoro ethylene) bag, the carbon content of which had to be taken into consideration at the calculation of that of the Ti meshes.

Samples cut from the catalyst mesh about 50–250 mg of each were analyzed with prompt gamma activation analysis (PGAA) [15], a nuclear analytical technique for non-destructive determination of elemental compositions. The samples were irradiated in a neutron beam for 40–70 × 10³ s at the PGAA-NIPS facility [16] of the Budapest Neutron Center and the gamma-rays from the radiative neutron capture were detected with a Compton-suppressed HPGe detector. The energies and intensities of the peaks in the gamma spectrum were determined with the Hypermet-PC [17] program, whereas the analysis software Prospero [18] was used to calculate the concentrations. These are obtained as weighted averages from several analytical lines. Every step of the measurement and the evaluation can be described with statistical methods; therefore the uncertainties of the results can be readily estimated from a single measurement.

The distribution of the precious metal content of catalyst 1 in its surface layer was determined by LA-ICPMS (laser ablation-inductive coupled plasma mass spectrometry) (ELEMENT2 Thermo Electron Corp., laser ablation and inductive coupled plasma mass spectrometry). The surface morphology (for catalysts 1, 1(3), 4, 6, 7, 8, and 9) and composition (for catalysts 1, 1(3), 4, and 6) were investigated by SEM (JEOL JSM 5600 LV, scanning electron microscopy).

The surface composition and valence state of the constituents of these catalysts were analyzed by a KRATOS XSAM800 XPS (X-ray photoelectron spectroscopy) machine using an Al K α source with 120 W X-ray power and 40 eV pass energy. To avoid any artifacts the catalysts were placed onto the XPS sample holder and analyzed in the form "as received" or "as prepared". The commercial sample was additionally reduced in situ at 500 °C in hydrogen flow at atmospheric pressure for 1 h in a catalytic reactor attached to the XPS machine. The VISION software from KRATOS was used for spectrum fitting and calculation of surface compositions. Since the Ru3d spin pair and the C1s peak overlap, the position, FWHM and area of the Ru 3d_{3/2} peak was constrained to the Ru3d_{5/2} peak. C1s at 285 eV and Ti⁴⁺2p_{3/2} at 458.8 eV were used for charge compensation.

2.3. Oxidation procedure

The samples were oxidized in a 850 ml stainless steel high pressure autoclave equipped with a magnetic stirrer (700 rpm), at 230 °C and 200 °C temperature and 50 bar total pressure for 5 h. The real wastewater sample 100 g (our code 5797, COD (chemical oxygen demand) value 178183 mg/L, TOC (total organic carbon) value 52850 mg/L) was mixed with NaOH solution until pH 14 and then it was diluted to 500 g (COD 35637 mg/L, TOC 10570 mg/L) and was subsequently oxidized. The premise of getting real wastewater sample from our partner pharmaceutical company was that we

would not publish the content of their wastewater. So the dilemma emerges, –what is more important, to be able to test our catalysts with a real process wastewater, or –to publish what kind of compounds are present in this wastewater. What we were allowed to publish were the COD and TOC values and that our sample was toxic and non-biodegradable and after oxidation it became biodegradable.

The starting pH of the reaction mixture was at pH 14 or 13, which decreased till the end of the oxidation to 9 or 8 because of organic acid and CO₂ formation. We have found the basic pH advantageous from the point of view of corrosion and catalyst leaching also.

The Na-phenolate solution was prepared by dissolving 18.8 g phenol and 8 g NaOH in 2 L distilled water (COD 21194 mg/L, TOC 7453 mg/L). Each time 500 g sample was introduced into the reactor. After loading the basic waste water samples or phenolate solution into the autoclave, it was pressurized with oxygen to 10 bar and under constant mixing heated up to the desired 200 °C temperature, the pressure set with oxygen to 50 bar and carried out the oxidation, keeping the pressure at 50 bar introducing oxygen into the reactor. Samples were taken periodically and then analyzed, the first sample was taken 1 h after the attainment of the desired reaction temperature.

In the case of CWO experiments, the monolith catalyst was rolled and placed into the autoclave (standing against the inner wall) before filling the reactor with wastewater. For determining the conversion-time relationship, liquid samples of approximately 3 ml were periodically withdrawn from the reactor through a tube located at its bottom. The outer section of the tube was water-cooled in a jacket for decreasing the sample temperature. Before taking each sample, the dead volume of the tube (about 7 ml) was disposed of, that is why it was necessary to work at least with 200 ml reaction mixture. Since the applied oxidation procedure is a batch-wise reaction in an autoclave under high pressure, the majority of volatile compounds and the formed CO₂ are dissolved in the aqueous phase, the latter as carbonate at the basic pH.

Prior to oxidation experiments the COD, TOC, pH values of the model and real wastewater samples were measured.

2.4. TOC, COD measuring methods

Liquid samples taken from the reactor during the CWO experiments were analyzed measuring their TOC and the COD values. The TOC was determined by a Shimadzu TOC analyzer whose operation was based on catalytic combustion and non-dispersive infrared (NDIR) gas analysis. TOC values were obtained by subtracting measured inorganic carbon (IC) from measured total carbon (TC). COD was determined by the standard dichromate method.

3. Results and discussion

3.1. Catalyst characterization

The Ru, Ir, Pd (Ta), other metal and carbon content of the mesh catalysts are shown in Table 1, as determined by PGAA. The geometric surface area of the Baoji Ti mesh is 1.5× higher, but the amount of Ru (0.1–0.15 g) and Ir (0.26–0.29 g) in the commercial mesh (samples 1 and 1(2)) are not far from the amounts found in the samples of our preparation (Ru 0.19 g, Ir 0.17 g in 4, Ru 0.19 g in 6, Ru 0.17 g, and Ir 0.09 g in 8) calculated from the percentage metal content and the mass of the meshes. So the catalytic activities of both meshes can be compared. The metal content differences between the two samples of the same mesh can originate from the non-uniform thickness of the precious metal oxide layer.

SEM showed the different structures of the active layer of the coated meshes. On the chemically purified Ti mesh the Ru, Ir metal

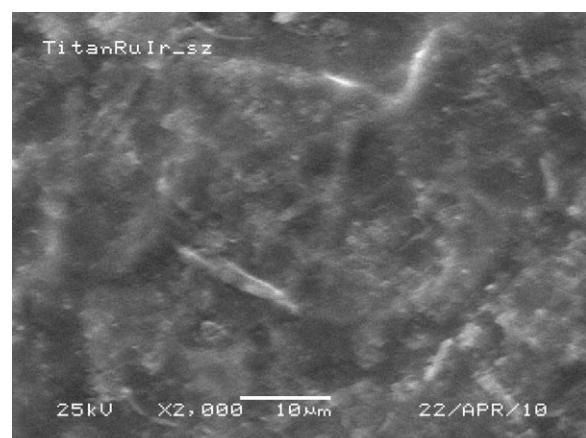


Fig. 1. SEM picture of mesh 4.

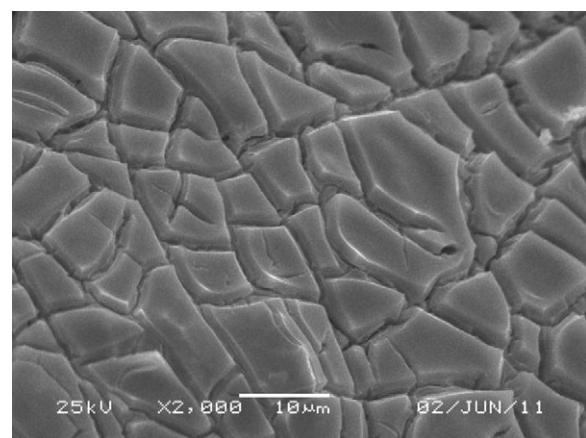


Fig. 2. SEM picture of mesh 1.

oxide layer is continuous, (Fig. 1), on the mechanically purified Ti mesh it is fragmented, similarly to the commercial mesh (Fig. 2). The surface analysis indicates the presence of both Ru and Ir besides Ti (Fig. 3). The SEM pictures and surface analysis of mesh 1 and 1(3) (Figs. 4 and 5) indicate that after longer use the surface is covered with precipitates, mainly iron and silicon, supposedly in their oxides. These meshes were used in WO of different real wastewaters, which contained Fe ions (detected by XRF) [13–15] and some of which contained silicates as well, coming from clarifying applied in the synthesis where they originated from. The PdO layer of mesh

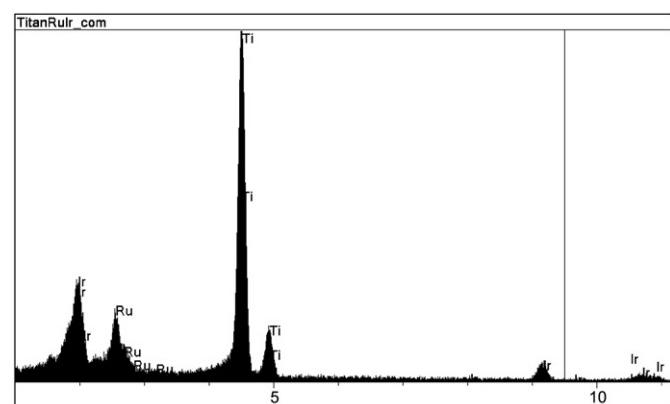


Fig. 3. Surface composition of mesh 1 determined by SEM, energy (keV) vs. intensity (arbitrary units).

Table 1
Composition of monolith catalyst samples.

Sample no.	Added components	Ru mass (%) ^a	Ir mass (%) ^a	Pd mass (%) ^a	Cd (ppm)	V (ppm)	Cr (ppm)	Ta (ppm)	C mass (%) ^d
1	Ru, Ir	0.14	0.35		3				n.d.
2	Ru, Ir	0.21	0.40						3
1(3) ^b	Ru, Ir	0.20	0.23		1				2
4	Ru, Ir	0.11	0.1						n.d.
4(5) ^c	Ru, Ir		360 ppm		0.5				4
6	Ru	0.11				210			n.d.
7	Pd			0.12		230			3
8	Ru, Ir	0.1	0.052		0.1	340	430		n.d.
9	Ir, Ta		330 ppm			200		19	3

^a Calculated on Ti mass.

^b After 170 h operation.

^c After 100 h operation.

^d 60–150% possible error, n.d.: no evaluable data.

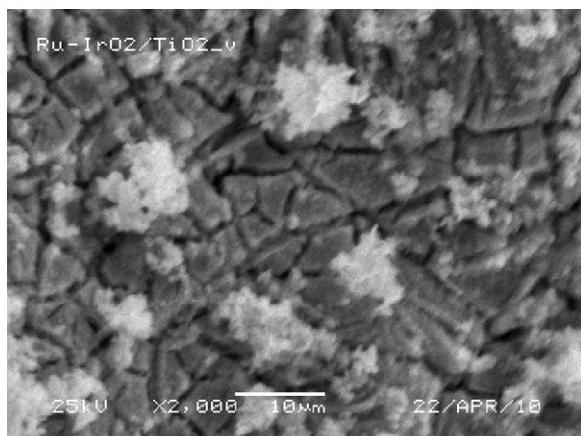


Fig. 4. SEM picture of mesh 1(3).

7 deposited on the chemically purified Ti mesh is fragmented contrary to Ru and/or Ir oxide, our experience was that this catalyst easily lost the precious metal oxide layer even on weak mechanical effect. The commercial catalyst is more resistant against leaching, more stable than our own one. XPS data (surface atomic ratio values of Ru/Ir/Ti in Table 2) can serve an explanation, both Ru/Ti and Ir/Ti surface ratio for the commercial catalyst are much smaller than for catalysts prepared in our laboratory, in spite of the similar overall mass % of this metals determined by PGAA. This is possible if the surface TiO₂ layer on the Magneto Ti mesh is artificially thickened. After depositing the Ru and Ir oxides on it, the resulting titania supported precious metal oxide catalyst layer resembles more a supported titania catalysts with smaller active phase content. On

Table 2
Surface ratio of components determined from XPS.

Catalyst	Ir/Ru	Ir/Ti	Ru/Ti	Remarks
1	5.0	0.11	0.022	Usual Ti peaks
1(3)	–	–	–	Several unknown peaks
4	1.6	0.73	0.44	Unusual Ti peak
8	1.5	0.67	0.46	Unusual Ti peak

the other hand the catalysts of our own preparation are based on the purified and self-oxidized Ti, which has a relatively thin oxide layer on its surface. The multiplied impregnation with the Ru and Ir salt solutions and the calcination resulted in a thicker precious metal oxide layer, with less surface titania content and less resistance against corrosion and abrasion. In order to increase stability of the latter, further experimentation is needed. The carbon content of the fresh and the used catalysts (Table 1) does not show any valuable tendency, we suppose that the carbon in the catalysts is in carbonates, formed during preparation and usage in the basic medium.

LA-ICPMS (Laser ablation-inductively coupled plasma mass spectrometry) gave the in depth distribution of surface concentration of the noble metal oxide components for mesh 1 (Fig. 6). The two oxides (Ru, Ir) are in nearly the same concentration on the targeted site and they appear at the same ablation time, which shows their similar concentration in depth of the surface layer.

XPS (Fig. 7) also gave information about the chemical valences of the catalytically active substances, they are definitely oxides of Ru and Ir on the oxidized Ti. The catalyst was fully oxidized in the form "as prepared". The overlap in the Ru oxide and C peaks and the high amount of surface carbon in the "as received" catalyst resulted in an uncertainty in the calculation of the surface concentration of Ru. To overcome this difficulty the sample was reduced in situ, resulting a shift of the Ru 3d_{5/2} peak to a lower binding energy and a separation from the C 1s peak. Simultaneously most of the carbon

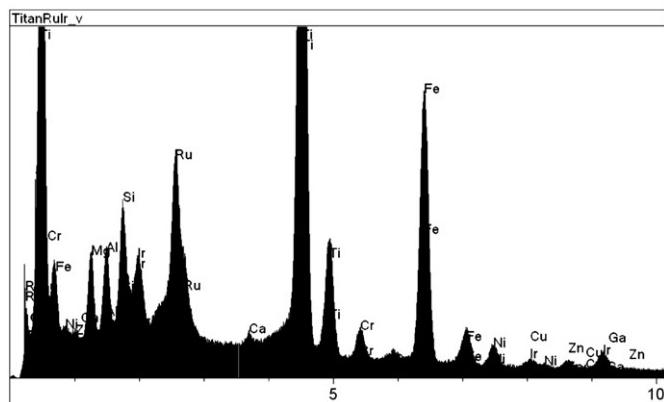


Fig. 5. Surface composition of mesh 1(3) determined by SEM, energy (keV) vs. intensity (arbitrary units).

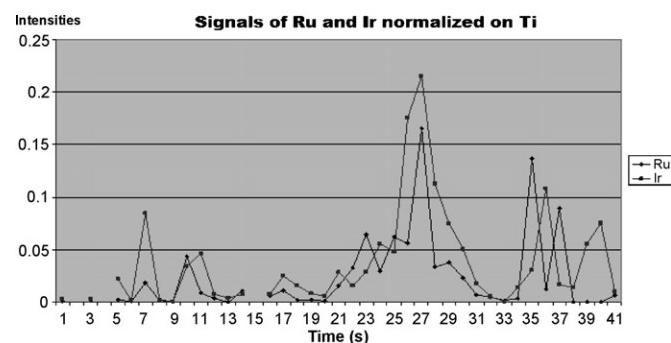


Fig. 6. LA-ICPMS spectrum of mesh 1, Ru and Ir signal intensities in the function of the time of ablation.

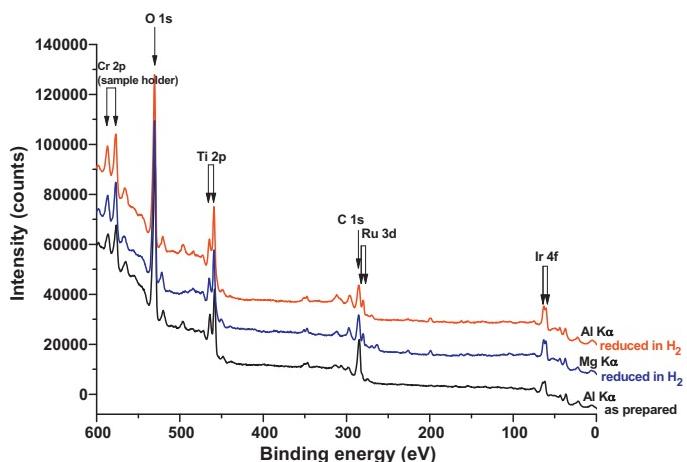


Fig. 7. XPS spectrum of mesh 1, lower curve: as received with Al K α , middle curve: after reduction in hydrogen with Mg K α , upper curve: after reduction in hydrogen with Al K α .

was removed by hydrogen and this also improved the reliability of the fitting.

3.2. Catalytic wet air oxidation experiments

The commercial Ti-mesh coated with ruthenium–iridium mixed metal oxide (Magneto Bv, No 1) which is recommended as anode material in highly oxidizing environments served as basis for comparing the activity of Ti meshes coated with different metal oxides prepared in our laboratories.

In wet oxidations there are two phases with respect to reaction rate, a first faster and a second slower one (in this period usually the carboxylic acids are oxidized) [15], thus quantifying reaction rates would not have been correct. Therefore an activity and stability sequence was established. In order to avoid false conclusion about activity, which usually changes faster in the very first phase of usage, the meshes were tested in detail after 10–15 h operation in WO. According to Figs. 8 and 9 the activity of meshes containing both Ru and Ir (1, 4, and 8) was highest, the commercial catalyst being the most active, as its geometric surface is smaller than that of the other catalysts, however the conversion values (TOC and COD decrease with catalysts 1, 4, and 8) are near to each other. Ru alone (6), Ir with Ta (9) and Pd (7) were less active. While the above discussed TOC decrease gives the carbon mineralization rate, the COD decrease which expresses the total oxidation rate (Tables 3 and 4)

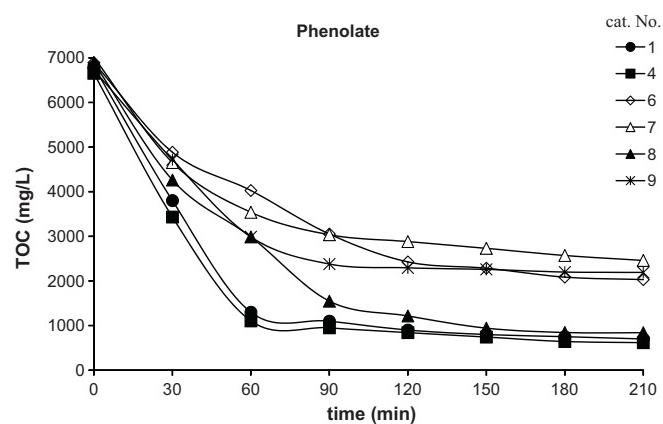


Fig. 9. TOC vs. time (200 °C, 50 bar) in wet oxidation of phenolate solution with different monolith catalysts.

Table 3

COD decrease with different catalysts in the oxidation of the real wastewater (230 °C, 50 bar).

Reaction time (min)	COD decrease (%)							
	Without catalyst	Catalyst 1	1(3)	4	6	7	8	9
60		55	29	59	48	43	62	32
180		85	39	89	56	68	87	47
300	38	95	41	97	62	80	95	48

Table 4

COD decrease with different catalysts in the oxidation of phenolate solution (200 °C, 50 bar).

Reaction time (min)	COD decrease (%)							
	Without catalyst	Catalyst 1	1(3)	4	6	7	8	9
60		70	40	79	59	51	58	67
120		90	70	90	67	72	82	74
210	54	95	75	95	73	76	87	77

of the same reactions, gave similar image: the activity sequence of the different catalysts was the same.

The experienced leaching and/or abrasion decreases the precious metal content (1(3), 4(5)) as well as catalytic activity. The commercial Ti-mesh (1) was used approximately for 170 h and its activity (Fig. 10) decreased after this usage together with its Ir metal

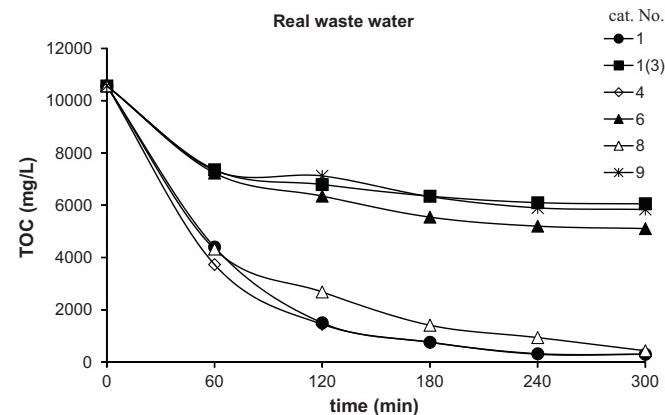


Fig. 8. TOC vs. time (230 °C, 50 bar) in wet oxidation of a real wastewater with different monolith catalysts.

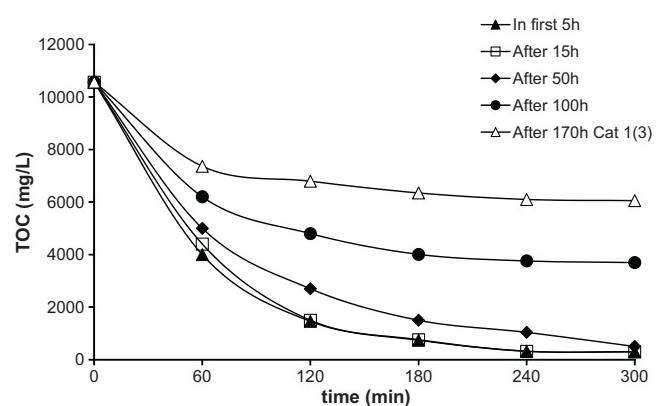


Fig. 10. TOC vs. time (230 °C, 50 bar) in wet oxidation of a real wastewater with catalyst 1 (commercial) after increasing time on stream, characterizing ageing.

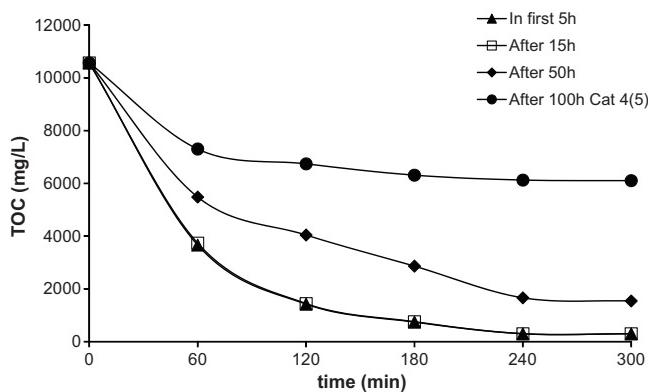


Fig. 11. TOC vs. time (230 °C, 50 bar) in wet oxidation of a real wastewater with catalyst 4 (own preparation) after increasing time on stream, characterizing ageing.

content (see Table 1, 1(3)). The catalysts prepared in our laboratory were less stable, 4(5) lost its Ru content according to PGAA, as well as major part of its activity (Fig. 11) after 100 h use.

4. Conclusion

The Ru/Ir oxide coated Ti monolith catalysts showed remarkable catalytic activity in wet oxidation both in the overall oxidation expressed by COD decrease and in the carbon mineralization expressed by TOC decrease. This was valid for the real pharmaceutical wastewater and for phenolate solution too. Meshes containing Ru, Pd and Ir oxide alone were less active than the Ru/Ir oxide together on Ti. This observation is in accordance with the electrochemical properties of the commercial mesh, which is offered by its producer for industrial hypochlorite production.

The commercial mesh was the most active and stable among the condition of wet oxidation, however loss of its precious metal content was observed during longer usage. The Ru/Ir monolith catalysts prepared in our laboratories had similar initial activities but they were less stable, the leaching and/or abrasion of the surface precious metal oxide layer was faster, independently of their structure being fragmented or continuous, depending on the preparation methods.

The loss of activity during longer usage can be the result of deposition of iron and silicon oxides too, showed by SEM analysis.

An important feature of the good catalytic activity of the Ru/Ir oxide coated Ti mesh can be the uniform distribution of the two oxides, as showed by LA-ICPMS. According to XPS results the upper surface layer of the catalysts is covered by a mixture of Ru-Ir-Ti oxide of approximately 0.1:0.02:1 atomic ratio for commercial

catalyst No1, and an 0.5:0.7:1.0 atomic ratio for catalysts No4 and 8 prepared in our laboratories. We suppose that such mixture of oxides with uniform distribution are the carrier of the good catalytic activity. The smaller surface Ru-Ir/Ti ratio of the commercial catalyst can be the reason of its greater stability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.08.004>.

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